Renewable and Sustainable Energy Reviews 30 (2014) 672–681

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Evaluation of infrared techniques for the assessment of biomass and biofuel quality parameters and conversion technology processes: A review

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ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form
24 October 2013
Accepted 11 November 2013
Available online 30 November 2013

Keywords:
Biofuel
Biomass
Optimisation
Control
Renewable energy sources

ABSTRACT

Rapid methods to characterise biomass for energy are needed due to the increasing use of biomass in the energy system and the expanding varieties of biomasses available. Chemical information on biomasses can be utilised in integrated management systems, allowing for the appropriate selection and optimum use of biomass to energy conversion techniques. Composition of biomass has important implications for optimisation of conversion processes such as pelletising/briquetting, combustion, gasification, pyrolysis and anaerobic digestion. There are opportunities to develop rapid spectroscopic techniques for both biomass to biofuel and biofuel to bioenergy process control. Rapid spectroscopic techniques and chemometrics may also be used to predict the key biomass and biofuel parameter calorific value and could be used to improve energy crop growing programmes. This review brings together the reported uses of infrared spectroscopic analysis coupled with chemometric techniques which have been applied to optimising biomass to biofuel and bioenergy conversion processes.

Contents

Abbreviations: EU, European Union; IEA, International Energy Association; Mtoe, million tonnes of oil equivalent; GHG, greenhouse gas; MC, moisture content; AC, ash content; CV, calorific value; AD, anaerobic digestion; PAT, process analytical technology; NIR, near infrared; PLS, partial least squares; BPLS, bi-orthogonal partial least squares; FTIR, Fourier transform infrared; PCA, principal component analysis; TG-FTIR, thermogravimetric Fourier transform infrared; OPD, optimal population density

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1364-0321/$ - see front matter
http://dx.doi.org/10.1016/j.rser.2013.11.006

1. Introduction

1.1. Biomass for energy production

Economies worldwide face two central energy challenges: securing the supply of reliable and affordable energy, and achieving the transformation to a low-carbon, high-efficiency and sustainable energy system [1]. An important step in decreasing the levels of greenhouse gases in the atmosphere is to increase the contribution of renewable energy in the energy mix [2]. In the European Union (EU) wood pellet demand grew to about 11 million tonnes in 2010, an increase of 7% on the previous year [3]. In 2013, the International Energy Association (IEA) estimated the global primary energy consumption for the year 2012 at 12476.6 Mtoe (Million tonnes of oil equivalent) [4]. Fossil fuel sources amounted to 87 (10,847.7 Mtoe) of this total with oil having the biggest share (33.1%), followed by coal (29.9%) and gas (24%). Nuclear and hydroelectric sources amounted to 4.5% and 6.7%, respectively [4]. Given that sources of fossil fuel reserves are being depleted and the greenhouse gases emitted through their combustion is leading to an accelerated change in global climatic conditions [5,6], alternative sources of energy will be needed in the medium to long term. Legislative requirements such as the Kyoto Protocol, the Irish Government's Energy White Paper and the EU Climate and Energy Legislative Package all call for a reduction in greenhouse gases (GHG's) and more emphasis to be placed on the use of renewable forms of energy [1,7]. Of the alternative sources available biomass plays an important role as it can be utilised in existing power generation facilities by co-firing the feedstocks alongside fossil fuels to reduce emission levels of major pollutants such as carbon dioxide, nitrous oxides and sulphur oxides [8–10].

It has been recognised that dedicated energy crops could provide a significant contribution as a major global primary energy source [11–13]. The dedicated bioenergy crops that have been widely investigated are switchgrass (*Panicum virgatum*), *Miscanthus* × *Giganteus* species, and short rotation woody crops i.e. willow (*Salix* species.) and poplar (*Populus* species) [14–17], while microalgae has emerged recently as a potential new bioenergy resource [18]. Switchgrass, which is native to North America, is a C_4 perennial grass which can be harvested twice a year. Biomass yield has been reported to range from 4.5, on marginal land, to 23 dry t ha^{-1} $year^{-1}$ in Alabama alone and an overall US average of 11.2 dry t ha^{-1} $year^{-1}$ [19]. Numerous factors can affect switchgrass productivity, including soil texture, nutrients, pH, and slope [20]. Economic analysis of switchgrass production in the USA indicate that production costs may be halved if the yield could be increased from 10 to 30 Mg ha^{-1} through genetic improvement, intensive crop management, and/or optimised inputs [21].

Miscanthus × *Giganteus* is also a C_4 perennial grass which can grow to over 3.5 m in height. *Miscanthus* × *Giganteus* is native to East Asia and was introduced to Europe from Japan in the 1930s [22]. Research has indicated successful *Miscanthus* × *Giganteus* establishment is related to an adequate soil moisture content (MC) and appropriate rhizome storage [23]. Indeed care must be taken to ensure that rhizomes do not dry out during harvest, transport or planting as this has been linked to poor establishment rates [22,23]. Willow is a perennial woody crop native to northern temperate zones. It grows up to 8 m in height and is usually harvested on a two to three year cycle. Some of the major contributing factors in poor establishment or yield include poor weed control and diseases such as *Melampora* rusts [24]. But it is not just woody biomass and grasses that can be used as energy crops. The use of microalgal cultivation for energy purposes is another emerging sector [18,25]. Microalgae are unicellular organisms that are typically photosynthetic and found in marine and freshwater environments. They have a high growth rate with higher biomass productivity and oil yield compared with other oil crops, which demonstrates its potential for production for energy purposes [25].

Variability in crop establishment and yield on a commercial scale will affect the economic return growers can expect and hence can be a barrier to the increased use of dedicated bioenergy crops. Therefore technologies which can assist producers in ensuring good crop establishment and achieving high productivity will be one critical tool to assist in the wide spread success of dedicated bioenergy crops. Remote sensing technologies can provide timely and accurate information which can be employed for crop management and to assess actual crop conditions [26]. Numerous vegetative indices have been developed using spectral remote sensing to quantify various agronomic parameters, e.g., leaf area, crop cover, biomass, crop type, nutrient status and yield [27]. Provision of important crop parameters is critical for optimising crop management and harvesting processes. Ehlert et al. [28] stated that sensors for measuring such parameters with an acceptable accuracy, high reliability and in a cost effective manner are essential. Rapid sensing techniques which can provide valuable information for crop management can include remote sensing and vehicle based methods. Such approaches take into account in-field spatial variability, thereby offering the potential to reduce input costs, optimise the use of inputs and reduce environmental impacts [29]. The compositional variances within many crops can often be difficult to control [30]. However if the composition of a given feedstock can be measured in real time that information could be used to adjust process conditions for optimal conversion of the biomass to energy.

Utilisation of sustainable agricultural crops and residues as sources of renewable energy can be further optimised using infrared spectroscopy within the ‘biomass to bioenergy’ chain. The conversion of biomass to energy is influenced by the type of feedstock, its physical characteristics and chemical composition [31,32]. Chemical composition of biomass fuels influences the choice of conversion technology suitable and process control in the selected conversion technology [33].

1.2. Biomass to biofuel conversion

1.2.1. Pelleting/briquetting

There has been increasing interest in biofuel pellet production for both domestic and industrial use in recent years [31]. Biofuel pellet production has grown rapidly in Europe, Northern America and China in the last few years [34,35]. There is a growing market for biofuel briquettes and pellets since biomass pellets offer advantages such as easy storage and transport, as well as lower pollution, lower dust levels and higher heating values than previously attainable [36]. Rhen et al. [37] reported that pellets offer the same advantages for automation and optimisation as the petroleum-derived fuels, with comparatively high combustion efficiency and low levels of combustion residues compared to traditional firewood. With this growth in pellet production and increasing varieties of biomass used in their production there is a need for rapid quality control techniques. Tabares et al. [38] reported the densification of biomass would help improve its behaviour as a fuel by increasing its homogeneity and allowing a wider range of lignocellulosic materials to be used as fuel.

MC is considered the principal parameter of importance in biomass chips and pellets for a number of reasons [39]. High MC in biomass chip piles can result in self-combustion of the pile due to elevated temperatures caused by increased microbial activity [40]. If the MC of the chips being fed into the pellet press is too low the friction between the particles and the die will increase the required energy to expel the material from the die or cause blockages

resulting in increased pelletiser downtime; low MC will also result in pellets with a low durability quality [39,41]. Low durability in pellets leads to high dust emissions, feeding problems in boilers, and an increased risk of fire and explosions during pellet handling, storage and transport [42]. Pellet durability is directly correlated with MC up to a maximum MC value for the biomass; too high MC results biomass not binding to form pellets [39].

Ash content (AC) of solid biofuels effects quality and quantity of combustion [43]. Monti et al. [43] reported that calorific value (CV) of energy crops negatively correlated with AC; in the study of six energy crops it was found that with a 0.2 MJ kg^{-1} decrease in the CV there was a corresponding 1 g 100 g^{-1} increase (on a dry basis) in AC. Ash from biomass combustion is made up mainly of inorganic elements such as sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca) [44,45]. High percentages of K and Ca in solid biofuels are responsible for lowering the ash melting point which can lead to combustion problems such as fouling, slagging and corrosion [45].

1.2.2. Combustion

The heating value of a biomass type, more often known as the CV, is a measure of the amount of heat energy released from a material when combusted (in the presence of oxygen). When comparing different biomass types the CV is widely similar at 18 MJ kg^{-1}, when samples have low moisture and ash contents [33]. As mentioned above for the combustion of pellets, variable MC, AC and lignocellulosic contents can cause the CV of biomass to differ greatly [46,47]. A feedstock with a less variable CV for combustion in a power plant will result in more stability and fewer emissions [45]. CV is also negatively correlated to the MC, as O–H bonds contain significantly less chemical energy compared with C=C and C–C bonds [46], therefore the greater the level of O–H bonds (in other words the higher the MC) in a substance, the lower the CV of that material. This lower CV is due to part of the heat released during combustion being used for evaporation of moisture from the feedstock, it has also been reported that materials with a high MC have problems with ignition which may lead to inefficiencies during combustion [45]. End users of biomass feedstocks look for products with the highest possible CVs due to the fact that consumers are buying the product mainly for the chemical energy which is stored in the biomass and will be released during combustion. This makes the knowledge of CV of biomass chips and pellets of utmost importance.

Carbon content of biofuel is another characteristic of importance for combustion purposes. If too little air is supplied to the combustion chamber excess amounts of carbon monoxide emissions and unburned hydrocarbons due to incomplete burning of the material will occur [48]. If the supply of air is too high an increase of NO_x emissions is the result [48]. Fossil fuels such as coal are typically classified by their ‘coke concentration’ which is a measure of the amount of carbon in the material [31,45]. Biomass in general contains lower coke contents than fossil sources due to the higher levels of O (oxygen) and H (hydrogen) in cellulose and hemicellulose [31].

1.2.3. Gasification

Gasification is a clean, efficient process capable of advanced applications in developed countries and also for rural generation in developing countries [49]. It is a partial thermal oxidation process that results in a high proportion of gaseous product and low proportion of ash and char, thus giving a more marketable fuel, becoming one of the most efficient biomass mass to energy conversion processes and one of the best alternatives for reusing waste solids [50]. The general process has been summarised with the following equation:

$$\begin{aligned} &CH_xO_y\ (\text{biomass}) + O_2(21\%\ \text{of air}) + H_2O\ (\text{steam}) \\ &\quad => CH_4 + CO + CO_2 + H_2 + H_2O(\text{unreacted steam}) + C\ (\text{char}) + \text{tar} \end{aligned}$$

The gasification of lignocellulosic biomass has been attracting considerable attention from various thermo-chemical conversion technologies due to the high conversion efficiency [51]. Gasification of biomass can also help with bioremediation plans through converting biomass wastes into clean fuel gases and biofuels [50]. Oxygen or air can be supplied to the reaction as the oxidising agent [52]. For easier and more versatile use than that of the original biomass, the quality of the gas produced can be standardised so that it can be used to power gas engines, fuel cells or gas microturbines, adding value to low- or negative-value feedstocks [52].

Microturbine gasifiers are typically categorised into the four main types of fixed bed, fluidised bed, moving bed and entrained flow [53] as shown in Fig. 1. Fixed bed and moving bed types can be disadvantageous as large quantities of tar and char are often generated due to the low and non-uniform heat and mass transfer between the solid biomass and the gasifying agent within the reactor [54]. Fluidised bed gasifiers however, provide excellent mixing and gas–solid contact that enhances the conversion efficiencies and reaction rate. As well as this, the use of bed material as heat transfer medium and catalyst improves the quality and decreases the tar content of producer gas [55].

As well as the type of gasifier used, the heating process involved can have an effect on the quality of the resulting gas. Autothermal gasifiers produce the necessary heat for the reaction through the partial oxidation within the gasifier. This is advantageous as it keeps the energy requirements, and therefore costs, to a minimum. However, as in an allothermal gasifier, when the heat-of-reaction is supplied externally, though it may be more energy intensive, the air-driven combustion is de-localised and the product streams can then be kept separate, thus producing a higher quality gas [56]. A good example of an allothermal set-up is discussed by Shuster et al. [57]. A dual fluidised bed steam gasifier is presented, with separate combustion and gasification zones. The gasification zone was fluidised with steam at 400 °C, while combustion of part of the product gas and char was carried out in another chamber to generate the heat. This allowed for greater control of the gasification temperature and fuel oxygen content, which were found to be the most significant factors in terms of chemical efficiency of the gasification [57]. Similarly, Kirnbauer et al. [58] demonstrated the use of a dual fluidised bed, where olivine was used as the bed material in this study. Also consisting of separate but connecting gasification and combustion reactors, the gasification reactor is fluidised by steam and the combustion reactor fast-fluidised by air, with the bed material circulating between the two reactors to transfer the heat. As well as using fluidised bed systems, allothermal gasifiers can employ liquid metal heatpipes to allow for the high heat transfer from the combustion chamber to the gasifier [59,60].

The importance of infrared spectroscopy to these processes is that it has the potential to further improve the efficiency of microturbine gasification technologies through the real time measurements of certain components it allows for; for example, control of CO formation in lignin gasification [61].

1.2.4. Pyrolysis

Pyrolysis for charcoal production is not a new technique but it is only in the last 3 to 4 decades that fast pyrolysis at very short reaction times and moderate temperatures of around 500 °C has become of considerable interest in terms of biomass to biofuel purposes [62]. This process can directly give high yields of liquid

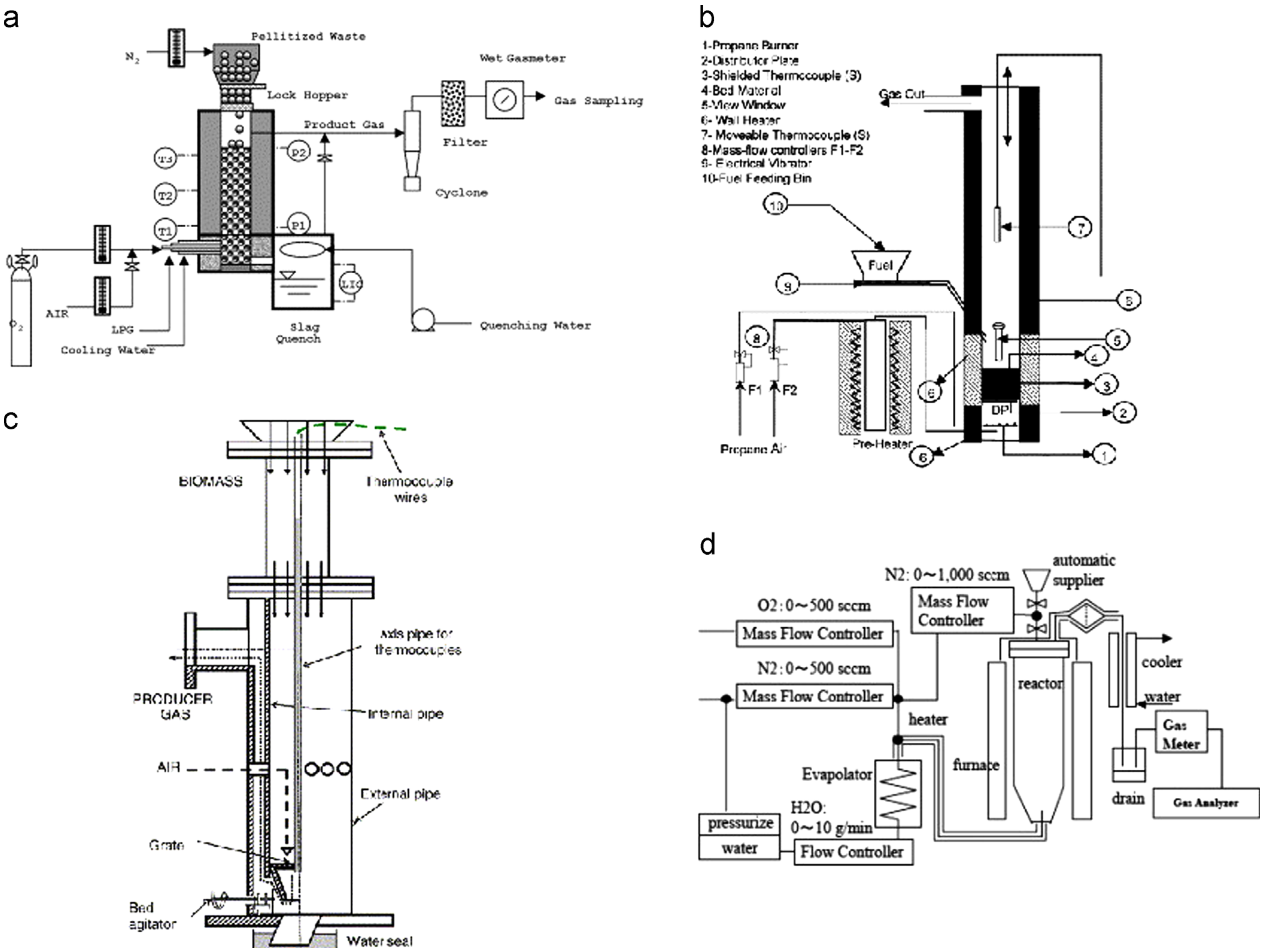

Fig.1. Typical layout of (a) fixed bed [110], (b) fluidised bed [111], (c) moving bed [112] and (d) entrained flow gasifiers [113].

product up to 75% which can then be used directly in numerous applications such as use as a biofuel [63]. Similarly to gasification, this technology offers the advantages of improved efficiency, environmental acceptability and versatility as virtually any type of biomass can be considered [63].

Pyrolysis is the thermal decomposition that occurs in the complete absence of oxygen. At lower temperatures and with longer residence times the production of charcoal is favoured, as opposed to gases when temperatures are high and residence times are longer, whereas moderate temperatures and short vapour residence time are optimum for producing liquids [62]. Liquid production from fast pyrolysis is currently of particular interest as the liquid can be stored and transported, and then used for energy, chemicals or as an energy carrier [62].

In terms of fast pyrolysis, biomass tends to decomposes very quickly and generate vapours and aerosols as well as some charcoal and gas. After it cools and condenses, a dark brown homogenous liquid is formed which has a heating value about half that of conventional fuel oil [64]. A high yield of liquid is obtained with most biomass feeds low in ash content [62]. The liquid yield as well as depending on the temperature and residence time also depends on the char and ash content as these two can have a catalytic effect on vapour cracking [64]. Drying the feed to typically less than 10% is necessary for fast pyrolysis processes as this will ensure small enough particle size for rapid reactions and efficient separation of the char and liquid [64].

1.2.5. Anaerobic digestion

Agriculture is being forced to become more efficient than ever before, to produce higher quality, safer foods while maintaining environmental quality. Greater management and control of the generated wastes also is of concern and thus effective monitoring technologies and processes are essential [65].

Much of this waste can be dealt with by anaerobic digestion (AD); however as with most bioprocesses it is a highly complex process due to high dimension, nonlinearity and dynamical characteristics. Ability to control bioprocesses accurately and automatically at optimal states is of considerable interest to many fermentation industries because it can reduce production costs and increase yield while at the same time maintaining a high quality metabolic product [66]. New, rapid and inexpensive methods that monitor the chemical composition of corn stover and corn stover-derived samples are a key element to enabling the commercialisation of processes that convert stover to fuels and chemicals [30].

The treatment of organic substrates such as sewage and animal manures, industrial effluents and solid substrates (agricultural residues, energy crops and food wastes) by the biochemical technological process of AD involves the degradation and stabilisation of complex organic matter under oxygen-free conditions by a collection of various anaerobic microorganisms [67]. The result is the production of an energy-rich biogas with a high proportion of methane, which can then be used as renewable energy to replace fossil energy sources [68].

It has been successfully implemented in the treatment of a number of wastes including food wastes, agricultural wastes and wastewater sludge, due to its chemical oxygen demand reduction capacity and biological oxygen demand reduction capacity from waste streams and producing renewable energy [69]. The process has the advantages of being able to successfully treat wet wastes of less than 40% dry matter [70] and minimise odour with 99% of volatile compounds decomposed [71].

1.3. Infrared spectroscopy

Within the last five years a new strategy for process optimisation and control emerged, namely the Process Analytical Technology (PAT) initiative [72]. This strategy aims to move from a paradigm of 'testing quality in' to 'building quality in by design' [72]. It has been widely adopted within the pharmaceutical and petrochemical process industries. To meet the objectives of PAT, real time sensing techniques are employed to control pre-determined critical control parameters throughout the processing chain. PAT can be defined as the optimal application of technologies in feedback process-control strategies, information management tools, and/or product-process optimisation strategies [73]. Recently, there have been significant advances in process sensors and in model-based monitoring and control methodologies. Improvements in process efficiency, reduced product variability and enhanced process understanding are some of the benefits arising from the introduction of a PAT strategy in the biomass-to-energy sector [74,75]. The adoption of a PAT to biomass-to-energy conversion processes will enable the optimisation of these processes. Such technologies would need to provide accurate, repeatable and timely measures of biomass parameters throughout the biomass-to-energy chain [72]. Application of appropriate sensing technology or practice will be key to the successfully implementation of integrated biomass management systems [76,77].

Near- and mid-infrared spectroscopy has been widely employed in a variety of sectors including the agricultural, food, and pharmaceutical industries for control and monitoring operations [78,79,80]. The near-infrared (NIR) region of the electromagnetic spectrum lies between 750 and 2,500 nm with the mid-infrared region between 2500 and 25,000 nm (i.e. 4000 to 400 cm^{-1}). Spectra are produced as the result of the absorption of radiation in these regions of the electromagnetic spectrum. Such spectra of a compound can reveal information pertaining to the molecular bonds present and hence provide details of its molecular structure. Therefore infrared spectroscopy may be used in both the qualitative and quantitative analysis of a product or process [81].

There are many optical methods that can and have been applied to biomass analysis. For example, Baumkahl and Karellas [82] investigated the use of UV and fluorescence spectroscopy for tar analysis from biomass gasification. While this study demonstrates the promise of these technologies for tar analysis discussed here, there are still limitations. For deep-UV (265 nm) the special requirements on optical components, for near-UV the ability to only induce fluorescence in higher tars, and overall the relatively high costs of many of the test set-ups described here may prohibit them from being more attractive for industrial applications [82].

Table 1
A summary of some of the key studies using infrared spectroscopy for organic matter, biomass, biofuel analysis, monitoring and optimisation.

Author	Technology	Wavelength range (nm)	Material examined	Properties predicted
Sanderson et al. [85]	NIRS	1100–2500	Wood; herbaceous feedstocks	Ethanol extractives; ash; lignin; uronic acids; arabinose; xylose; mannose; galactose; glucose; C; H; N; O
Bassilakis et al. [98]	TG-FTIR	Not reported	Wheat straw; biomass model compounds	Biogas process methanogen density
Zhang et al. [102]	Not reported	1100–2500	Pelletised *Miscanthus* × *Giganteus*; wood	Product-evolution data
de Jong et al. [100]	TG-FTIR	Not reported	*Triticum aestivum*	Tar; char; CH_4; CH_2O; CH_3OCH_3;CO; CO_2; HCN; HNCO
Hames et al. [30]	NIRS	400–2500	Corn stover; corn stover-derived samples	Lignin; glucan; xylan; protein; acetyl; galactan; arabinan; mannan; uronic acid
Cao et al. [103]	FT-Raman spectra	1064 (excitation)	Wheat	Lignin; cellulose; hemicellulose
Kelley et al. [86]	NIRS	500–2400	Agricultural biomasses; residues	Classification; lignin; glucose; xylose; mannose; galactose; arabinose; rhamnose
Lestander et al. [46]	NIRS	780–2500	Norway spruce	Moisture; ash; calorific value
Acuna and Murphy [89]	NIRS	400–2500	Wood	Density
Sandnes et al. [104]	NIRS	Not reported	Algae	Algal biomass density
Jin and Chen[90]	NIRS	900–1430	Rice straw	Total ash; insoluble ash; moisture; cellulose; hemicellulose; Klason lignin
Baptista et al. [109]	NIRS	833–2500	Biodiesel	Esters content linolenic acid methyl esters (C18:3) for myristic (C14:0); palmitic (C16:0); stearic (C18:0); oleic (C18:1); linoleic (C18:2) acid methyl esters
Baptista et al. [108]	NIRS	833–2500	Biodiesel	Iodine; cold filter plugging point; kinematic viscosity at 40 °C; density at 15 °C
Huang et al. [91]	NIRS	800–2500	Straw	Heating value
Huang et al. [92]	NIRS	400–2500	Rice straw	Moisture; ash; volatile matter; fixed carbon; calorific value
Labbe et al. [88]	NIRS	350–2500	Biomass	Ash; char content
Allison et al. [44]	FTIR	2500–16500	North American tuft grass; reed canary grass	Nitrogen content; alkali index
Allison et al. [61]	FTIR	5000–10000	Grasses (*Lolium, Festuca and Dactylis*)	Lignin; hydroxycinnamic acidtotal ferulate monomers plus dimers; *p*-coumarate; ferulate dimmers
Lestander et al. [93]	NIRS	400–2500	Norway spruce; Scots pine	Moisture content; blends of sawdust; energy consumption of the pellet press
Wiley et al. [79]	NIRS	1100–2500	Barley	Nitrogen; protein composition
Fagan et al. [76]	NIRS	400–2498	*Miscanthus* × *Giganteus*; SRCW	Calorific value; moisture; ash; carbon
Everard et al. [75]	vis-NIRS	400–1000	Milled *Miscanthus*; milled SRCW	Moisture; ash; carbon
Everard et al. [77]	vis-NIRS	400–1680	*Miscanthus*; SRCW	Calorific value

NIRS, near infrared; FTIR, Fourier transform infrared; FT, Fourier transform; TG-FTIR, thermogravimetric Fourier transform infrared; SRCW, short rotation coppice willow.

The application of NIR spectroscopy within industry has been made possible by the development of more robust NIR instruments and the use of optical fibre that allows online monitoring [83]. Important to the development of NIR spectroscopy has been the development and acceptance of multivariate data analysis which is essential for many NIR applications and especially for a complex bio-process [84]. Another valuable factor is that infrared spectroscopy can be applied to predict the composition of a wide array of biomass and biofuel types, including switchgrass, sugarcane bagasse, corn stover, Eucalyptus and American sycamore [14]. Particularly for the prediction of CV moisture, ash and calorific content it has already been seen to useful [46]. These and other examples will be discussed further in the following sections, with a summary of some of the key studies presented in Table 1.

2. Infrared spectroscopy for biofuel production from biomass

2.1. Biomass analysis

Matching the chemical composition of a biomass sample to its conversion efficiency is one of the primary goals for improvement programmes and for the determination of biomass quality feedstocks prior to use [44]. There is a clear need for methods which allow prediction and characterisation of chemical composition in a cost effective and rapid manner.

Many studies have been undertaken coupling NIR with partial least squares (PLS) regression for the prediction of these compositional characteristics. Sanderson et al. [85] applied NIR spectroscopy in conjunction with PLS regression for the prediction of the chemical composition of 121 woody and herbaceous feedstocks. This was a laboratory based study in which 20 samples were used to validate the calibration models. While lignin and arabinose could be predicted, mannose, galactose, C, H and O were not successfully predicted. NIR spectroscopy chemical prediction models for corn stover and corn stover-derived samples have also been developed. The overall results show that NIR spectroscopy could be used for the prediction of the chemical composition of a broad range of biomass feedstocks. However, the population size used here was still relatively small and so larger sample sizes would be needed for more robust models for commercial use or further research [85]. Further studies have gone on to provide evidence of the potential use of NIR spectroscopy in conjunction with PLS regression for the prediction of lignin, xylose, mannose, galactose, rhamnose [86,87], glucose, arabinose, [86] char [88] and ash content [87,88] of a wide range of woody biomass types. While the correlation coefficients of these properties varied somewhat, it was concluded that the models overall showed a reasonably good predictive ability and could be used for initial screening or were promising to develop higher quality models with more samples from a specific feedstock of interest [86,88].

Hames et al. [30] reported the success of using NIR spectroscopy and PLS multivariate analysis for corn stover and corn stover derived samples which allowed for the compositional analysis of hundreds of samples per day at a cost of about $10 each. The NIR with PLS rapid analysis method demonstrated here has shown to be effective and the suggested use in further projects that were otherwise too costly may now be achievable. Lestander and Rhen [46] also coupled NIR spectroscopy with PLS. Bi-orthogonal partial least squares (BPLS) regression was used to model the moisture and ash contents of 16 samples from Norway spruce trees that were artificially moistened to varying degrees. Gross CVs of these ground samples of the wood stems and branches were able to be successfully predicted with high accuracy and accounting for up to 99.8% of the reference variable variation. Both these studies show the usefulness of coupling PLS analysis with IR spectroscopy to provide an affordable and effective method for the prediction and compositional analysis of different biomass types.

As CV is one of the critical parameters of a biofuel, many other studies have also looked at the CVs of other woody biomass types. Everard et al. [75] looked at evaluating the gross CV of *Miscanthus* × *Giganteus* and willow in Ireland, using visible and near infrared spectroscopy in the range of 400–1100 nm. Coupled with PLS regression, spectroscopic analysis showed the potential of these spectroscopic methods for rapid biomass characterisation according to gross CVs. This verified their results from a previous study [76] which also showed high accuracy for predicting CV as well as the moisture content, while the accuracy of models for ash and carbon content was less so, but could still potentially be used in simpler screening applications. The use of NIR spectroscopy has been used to predict a wide number of properties from various biomass types, including both woody and non-woody species, and is suitable for both unprocessed and processed biomass [86]. In the logging industry there are a number of properties that need to be understood to evaluate the economics of any situation including stiffness, density, spiral grain, and extractives content, as well as those already discussed such as ash and moisture content [89]. Furthermore, real time assessment would be even more favourable to allow log supply managers make timely decisions. Acuna and Murphy [89] indicated that NIR spectroscopy allows for accurate prediction of the density of processed Douglas fir saw chips, reporting coefficients of determination between 0.89 and 0.95 for calibration models and between 0.56 and 0.85 for validation models. Thus NIR technology could be successfully used in the log harvesting industry to predict wood density.

A number of studies have also looked at the use of NIR for the prediction of CV, heating value, ash and moisture contents, etc. of straw biomass [90,91,92]. While NIR spectroscopy can be used to determine the nutritional quality of straws as an animal feed [90], straw can be also be used for energy production and similarly the quality parameters are of interest. And while Jin and Chen [90] focused on the prediction of rice straw quality as an animal feed, some of the parameters that needed to be predicted were the same as those of many biomass to energy studies (e.g. ash and moisture content). Hence NIR coupled with PLS was investigated and was shown to be an effective, rapid and accurate method for predicting lignin, cellulose, hemicellulose, and ash and moisture contents, with a coefficient of determination above 0.85 for all measured components. Straw biomass for heat and energy generation has also been investigated for the prediction of heating values [91,92]. Constructed validation models for each show satisfactory rapid prediction potential. The coefficient of determination for the NIR spectroscopy validation model for heating values was 0.96.

Other studies have shown that NIR spectroscopy and multivariate analysis can equally be applied to the prediction of parameters of grass species. Allison et al. [44,61] have looked at applying Fourier transform infrared (FTIR) spectroscopy to a number of grass species in a similar manner. FTIR spectroscopy coupled with PLS regression was shown to accurately predict the alkali index and nitrogen content of dried samples of switch grass and reed canary grass, which both influence the thermal conversion efficiency of the grasses [44]. In addition, the ash and carbon contents could also be predicted, as seen in studies discussed earlier. Allison et al. [61] reported that levels of lignin and hydroxycinnamic acid wall components were also able to be predicted with FTIR spectroscopy and PLS regression for three genera of forage grasses (*Lolium, Festuca and Dactylis*), as the accuracy of the test of predicted versus actual values was shown to be 92.8%.

Lestander et al. [93] observed the use of online NIR spectra from sawdust (from Norway spruce and Scots pine) for real time

predictions of MC, energy consumption of the pellet press and blends of the sawdust, on an industrial scale and while varying factors such as drying temperature. The results showed excellent calibration models for the observed parameters with the power consumption model accounting for 91% of the variation in the test set of experimental runs. Thus, an online NIR system could be a viable option and important tool for sawdust pelleting processes and other similar operations.

More recently, Everard et al. [75] investigated the potential use of online vis-NIR spectral sensing techniques in conjunction with chemometrics for the rapid analysis of the moisture, ash and carbon contents of *Miscanthus* and 2 varieties of willow. Principal component analysis (PCA) of the samples was able to successfully distinguished the different biomass types, while PLS regression gave strong predictions for the moisture and carbon contents (and the ash content to a lesser extent), opening up the possibility for a more efficient, higher quality pellet production system through online and real time characterisation of the pre-pelletised biomass.

In summary, calorific value, moisture content and ash content are some of the most important parameters that need to be determined for biomass quality. However, depending on the industry, biomass type or use, the prediction of several other quality indices (e.g. carbon content, density etc.) may also be desirable. Models for moisture content are based on the O–H and C–H overtones, i.e. between water and organic matter. Models for CV, on the other hand, involve O–H and C–O stretching as well as C=C bonds to some extent [46]. These studies, as well as others, show the possibility of using NIR in conjunction with multivariate analysis to accurately predict, in particular, the economically important properties.

Particularly in industry, rapid online characterisation is essential. If a non-homogeneous mix of biomass types is in use as an energy source, then the pertinent physical and chemical characteristics will be even more variable and therefore there will be the need for improved characterisation of these properties for optimal performance [94,95]. Most importantly however is the CV of a given feedstock, which is in turn influenced by the moisture and ash contents as well as the dry mass chemical composition. The use of NIR and multivariate analysis of biomass composition, now well established and proven to be accurate for a number of parameters, may be a preferable option for analysis compared to older methods which would have been slower, more expensive and not as effective [30].

2.2. Optimisation of conversion processes

Spicer et al. [96] carried out a purely economic assessment of several biomass types in Ireland (willow, *Miscanthus*, straw) for liquid biofuel production and the costs of various conversion processes. Results from this study showed that an intermediate conversion step (from fast pyrolysis) will create a significant increase biodiesel production cost. However, from these findings gasification and synthesis technologies can potentially produce economically viable alternatives to fossil fuels, as well as the potential for Fischer–Tropsch diesel produced to be cost competitive with fossil diesel equivalents, given government support. This shows that the potential is there for these biomass to energy processes but these processes need to studied and optimised for quality as well as cost. Some of the main conversion processes have been discussed above (e.g. pyrolysis, gasification, combustion, anaerobic digestion). There is a great deal of research currently being carried out in these areas as they are still not fully understood and need to be optimised in order to make biofuels competitive with fossil fuels and other forms of energy. For example, there exists the need for comprehensive biomass-pyrolysis models that could be used to predict the evolution patterns and yields of a number of volatile products in relation to the pyrolysis process conditions and the characteristics of the feedstocks in question. Some models have turned to using thermogravimetric Fourier transform infrared (TG-FTIR) analysis to generate input data under low heating rate conditions [97]. Bassilakis et al. [98] successfully developed TG-FTIR quantification routines for basic analysis of three compounds (xylan, chlorogenic acid, glucose) and wheat straw, which established the groundwork for further studies. Comparisons with other literature were made and showed the potential to provide good input data for the predictive modelling of biomass pyrolysis, despite the complexity of patterns and difficulty in interpretation [98]. More recently, the investigation of pyrolysis of rice straw and bran, as well as manure, for biochar production was evaluated [99]. Through the study of the individual conversion of the cellulose, hemicellulose and lignin of these materials, it was shown that these different biomass types displayed distinct thermodynamics characteristics. de Jong et al. [100] also investigated biomass pyrolysis using TG-FTIR analysis. This study looked at two types of biomass fuel (pelletised *Miscanthus* × *Giganteus* and wood) and the measurement of products under the heating rate profiles of 10, 30 and 100 °C min^{-1} and a final temperature of 900 °C. NIR analysis was able to predict the products HCN, HNCO and, to a lesser extent NH_3. The models produced for TG-FTIR product-evolution data were found to be generally good, however the model-predicted yields for some of the species didn't fit the experimental data at all of the heating rates. This problem may be resolved with further improvements in the models [100]. All of these studies [97–100] discuss different biomass feedstocks and their desired end products through pyrolysis. But they all focus on determining the optimal reaction kinetics of pyrolysis from FTIR results to maximise product yields and minimise secondary reactions. The thermal conversion characteristics, process time and the size of the precursor material all affect the pyrolysis process and from the examples listed above may need to be adapted to optimise the process, which may be determined by FTIR analysis.

Another biomass conversion process that is also still being researched into is optimising AD. The productivity of anaerobic digesters can be improved with the appropriate levels of microbial mass in the reactor, which in turn can be determined through the prediction of changes in the biomass [101]. Zhang et al. [102] investigated the possibility of using NIR for monitoring the density of methanogens in a system during biogas production. Using acclimated methanogens at fixed temperature and pH, the NIR absorption spectra were recorded, collected and examined with the resulting peaks found to be predominantly based on α-proteins and lipids from the methanogen cells' cytoplasm and membranes. As well as this, the methane fermentation was monitored using NIR on acetic acid as the substrate. The resulting NIR analysis was correlated to the methanogen density using PLS regressions with the resulting correlation coefficient of 0.99 and a standard error of prediction of 0.55 g l^{-1}. For acetic acid, the correlation coefficient was also 0.99 and the standard error of prediction 0.63 g l^{-1}. Methanogen densities up to 10 g l^{-1} were used in this study. Thus given the results above, it has shown that the methanogen densities and acetate concentrations of AD systems can be successfully monitored simultaneously. To optimise the AD process productivity, there needs to be an increase in the microbial mass and maintaining a high methanogen density, which in turn will cause changes in the biomass at a different rate that needs to be predicted and monitored [102]. Thus rapid measurements and online measurements become very important in the conversion process and these have been carried out in this study using NIR analysis.

Intermediary biomass products can also be subjected to monitoring during conversion processes for optimisation. Cao et al.

[103] investigated the use of FT-Raman spectra for *Triticum aestivum* treated with enzymes multicomponent cellulase and purified endoglucanase, which change the structure and properties of the biomass. These changes however depend on the composition and type of enzymes used. For example, endoglucanase contains less xylanase activity than that of the multicomponent cellulose and therefore the biomass samples subjected with endoglucanase were observed to have higher contents of lignin and hemi-cellulose, as determined by the FT-Raman spectra analysis [103].

Algal biomass is an area in which there is a particular need for online monitoring, with rapid growth and diurnal growth patterns [104]. Sandnes et al. [104] used NIR sensors for real time monitoring and for density controlled feedback in mass cultures in 200 l tubular biofences. With online data recorded and a programmable system, the optimal population density (OPD) is easier to maintain and higher biomass production levels can be sustained and harvested. Thus, the system could potentially be used to operate a dynamic density set point for algal cultures whereby the OPD varies as a function of ambient growing conditions [104]. However, there are few other studies in the area of the use of infrared spectroscopy for prediction and monitoring in microalgal systems. And while this is still a growing sector, this will need to be addressed to develop more advantageous systems.

With precursor biomass material variable in size and composition, the kinetic parameters of processes such as gasification and pyrolysis, the levels of microbial mass in AD or the type and amount of enzyme for enzymatic treatment of biomass, for example, will need to be modified such as in the cases above so that the conversion processes adapt to the changing feedstocks in order to obtain the optimal yields of the desired end products.

2.3. Biofuel analysis

As one of the main alternatives to fossil diesel, biodiesel is of growing interest and becoming more widespread due to it being safe to handle, biodegradable, renewable and having lower emissions [105]. Biodiesel is produced from the transesterification of a mixture of fatty acid methyl esters, which are derived from animal fats or vegetable oils, with the oils and/or fats reacting with alcohols in the presence of a catalyst [106]. The importance is ever greater with European governments targeting 20% of fuel use as biofuels for 2020 with biodiesel quality assessed using 25 analysed parameters under European Standards [107].

Thus, as with biomass analysis, biofuels need appropriate monitoring and analysis to determine quality for commercial and industrial purposes. Baptista et al. [108] applied the use of NIR spectroscopy to attempt to determine the iodine value and cold filter plugging point of biofuels, as well as the kinematic viscosity (at 40 °C) and density (at 15 °C). Qualitative analysis of the measured spectra was carried out using PCA and PLS, with calibration models developed. The results from this study showed that NIR spectroscopy may indeed be used to predict all of the above properties at laboratory scale and for industrial samples, with the potential for online monitoring for simpler and more affordable quality control purposes for the final product [108].

Another work reported the use of NIR to determine the ester content in biodiesel, as well as the ester content in linolenic acid methyl esters (C18:3) of the analysed biodiesel samples [109]. Calibration models were also obtained for the myristic (C14:0), palmitic (C16:0), stearic (C18:0), oleic (C18:1), linoleic (C18:2) acid methyl esters. Quantitative analysis of the observed spectra with PCA and PLS was again used to develop calibration models, with the resulting models confirming the potential for the use of NIR spectroscopy, in combination with multivariate calibration for the assessment of biodiesel quality in both laboratory-scale and industrial scale samples [109].

3. Conclusions

This review focuses on infrared spectroscopic methods for the characterisation of biomass and biofuels. The use of biomass and biofuel for energy purpose can be carried out in a number of ways such as combustion, gasification, pyrolysis, anaerobic digestion etc. The choice of which of these methods will depend on biomass/fuel type, economic and social factors and geographic considerations among others. The characteristics of these differing processes can vary greatly all need appropriate monitoring and analysis systems to achieve the most economically and environmentally favourable conditions.

Relevant studies advocate the potential use of infrared spectroscopic methods in integrated management systems for the appropriate decision making and optimisation. Many of the quality indicators of biomasses, intermediates and the final product biofuels can be predicted accurately, with continual research improving this accuracy of these methods. These parameters include calorific value, moisture, ash, carbon and nitrogen contents among others.

However, while some bioenergy production processes are now well understood and controlled, others are less so and need further research to optimise them. The benefits of rapid, online management systems are now well known, a wide number of methods have been used in these studies reviewed here. The appropriate use of infrared spectroscopy will depend on a number of factors such as the biomass type, conversion process, end product use and parameters of interest.

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